



Review

The efficiency and mechanisms of catalytic ozonation

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ABSTRACT

Catalytic ozonation has recently gained significant attention as an effective process used for the removal of organics from water. Unfortunately, despite increasing research efforts in the field of catalytic ozonation and the introduction of new catalysts, the mechanisms of catalytic processes are still largely unknown. An understanding of the mechanisms of catalytic ozonation is vital in order to introduce this technique in water treatment at an industrial scale. Therefore, the main aim of this paper is to provide a short overview of catalytic processes, their recent advances and to identify major directions taken to understand mechanisms governing catalytic processes utilised in water and wastewater treatment. Catalytic ozonation is considered to belong to Advanced Oxidation Processes. However, the results published by several research groups indicate that not all catalytic processes utilise the power of hydroxyl radicals.

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1. Introduction

Ozone is used as an effective oxidant in water and wastewater treatment and also air purification. The effective usage of ozone in all the above mentioned fields is vital and therefore extensive research aiming at the utilisation of catalytic ozonation has been undertaken. Two comprehensive papers were published by Oyama

[1,2] on the application of catalytic ozonation in air purification. Several applications of ozone in water treatment technology are subjects of discussion in many books [3–7]. It is a well known fact that ozonation can proceed via two routes: direct molecular ozone reactions and/or indirect pathway leading to ozone decomposition and the generation of hydroxyl radicals (OH•). Reactions of ozone with organic matter usually lead to the formation of aldehydes and carboxylic acids, both of which do not react with ozone. This is an important limitation of ozonation as total mineralization of organic matter is not achieved. Additionally, oxidative reactions

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Table 1
Homogeneous catalytic ozonation.

Catalyst	Organic compound	Reference
Mn(II)	Carboxylic acids (oxalic, pyruvic, glyoxalic, propionic, sulfosalicylic), N-methyl-p-aminophenol, atrazine, dinitrotoluene (DNT), dichlorophenol (DCF)	[13,21,23,24,26–29,41,42,164–167]
Mn(II), Fe(II), Fe(III), Cr(III), Ag(I), Cu(II), Zn(II), Co(II), Cd(II)	Humic substances	[13,23]
Mn(II), Fe(II), Fe(III)	Chlorobenzenes	[21]
Mn(II), Fe(II)	Simazine	[168]
Pb(II), Cu(II), Zn(II), Fe(II), Ti(II), Mn(II)	2-Chlorophenol	[169]
Fe(II), Fe(III), Mn(II), Co(II)	Lignin sulfonate	[170]
Ni(II), Fe(II), Mn(II), Zn(II), Sr(II), Cr(III), Cd(II), Hg(II), Cu(II)	1,3,6-Naphthalenetrisulfonic acid	[30]
Co(II)	Oxalic acid, pyruvic acid	[16,17,32]
Cu(II)	Oxalic acid, pyruvic acid	[19]
Mn(II), Fe(II), Fe(III), Zn(II), Co(II), Ni(II)	Azo dyes	[171]
Ce(III)	Phenol	[172]
Fe(III)	Oxalic acid	[18]
Fe(II), Cu(II), Co(II), Mn(II), Ni(II), Zn(II), Cr(III)	Carboxylic acids	[20]
Fe(II), Cu(II), Ni(II), V(V), Mo(VI)	Dinitrobenzene (DNB)	[31]
Mn(II), Fe(II), Mo(VI), Cu(II), Ni(II)	Benzoic acid	[173]
Mn(IV)	Propionic acid	[19]

with ozone are relatively slow and selective. Therefore, if the ozonation reaction is not satisfactorily fast, radical processes have to be implemented. Ozone decomposition in water is strongly pH dependent and occurs faster with an increase of pH. Reactions of radicals with organic and inorganic molecules are, as opposed to direct molecular ozone reactions, fast and non-selective. Recombination of hydroxyl radicals might also take place and might lead as a result to inactive moieties. Termination of the radical chain reaction leads to a decrease of ozone oxidative power. In contrast to ozonation alone, catalytic ozonation allows for the effective formation of hydroxyl radicals also at a low pH. Catalytic ozonation utilises catalysts in order to achieve controlled decomposition of ozone and hydroxyl radicals' formation. Therefore catalytic ozonation can be placed in the group of methods called advanced oxidation processes, although there are some exceptions observed. Catalytic ozonation should provide fast degradation of organic pollutants and also more effective mineralization of both micropollutants and natural organic matter.

The main aims of this paper are to provide a short overview of catalytic processes and to indicate new possibilities for effective water purification and wastewater treatment. This manuscript focuses on recent advances in the field of catalytic ozonation. In order to obtain additional information on catalytic ozonation, the reader is referred to a book written by Beltrán [8] and other reviews earlier written by Legube [9], Pirkanniemi and Sillanpää [10] and Kasprzyk-Hordern et al. [11]. Unfortunately, despite increasing research efforts in the field of catalytic ozonation, the mechanisms of catalytic processes are still largely unknown. Several catalysts have been proven to be effective in the enhancement of ozonation efficiency but the mechanism of such catalytic processes is still to be resolved. An understanding of the mechanisms of hydroxyl radicals' formation during catalytic ozonation is vital in order to introduce this technique to water treatment at an industrial scale.

Catalytic ozonation processes utilise several phenomena and can be divided into the following sub-techniques, which facilitate ozone decomposition and hydroxyl radicals' formation:

- *Homogeneous catalytic ozonation*: ozone decomposition is catalysed by transition metal ions.
- *Heterogeneous catalytic ozonation*: ozone decomposition is catalysed by solid catalysts.

Because catalytic ozonation should be characterised by higher efficiency of organic contaminants removal than ozonation alone,

the organic contaminants that are usually chosen for study are those which can be only removed via radical mechanisms. Among them are: oxalic, pyruvic, p-chlorobenzoic and 1,3,6-naphthalenetrisulfonic acid, nitro- and chlorinated aromatic compounds.

Another group of methods enhancing the ozonation process take advantage of the higher solubility and stability of ozone in non-polar media. These methods called two-phase ozonation can be undertaken in liquid–liquid or liquid–solid systems. Despite the fact that these methods aim at molecular ozone stabilisation, it has been shown that such processes can also support processes occurring via radical mechanisms [12].

The literature concerning catalytic ozonation indicates several controversies in this field. Frequently, the same catalysts, studied by different research groups, lead to different, sometimes contradictory results. This aspect of research in the field of catalytic ozonation is particularly emphasised in this manuscript. The verification of mechanisms governing catalytic ozonation seems to be particularly problematic, as the usage of catalysts in aqueous solutions will lead to competition between water, ozone and organic compounds for catalytic (adsorptive) active sites.

Several research groups have reported the high efficiency of catalytic ozonation in the removal of organic contaminants in water. There is, however, limited understanding of this technique as far as mechanisms of the process are concerned. There are therefore several questions that need answering in order to understand the processes occurring during catalytic ozonation and to apply this emerging chemical oxidation technique on a technological scale:

- It is not clear whether catalysts cause ozone decomposition leading to hydroxyl radicals formation (some published reports suggest mechanisms that are different from a radical pathway leading to hydroxyl radicals formation).
- It is not clear how ozone is decomposed on the surface of catalysts (several mechanisms are proposed and the major question that needs answering is whether hydroxyl radicals are formed directly due to ozone decomposition on the surface of catalyst or indirectly, as a result of secondary reactions).
- How do natural water constituents such as sulfates, phosphates, carbonates, bicarbonates and fluorides influence the catalytic ozonation process, e.g. catalytic activity?
- What is the long-term activity of catalysts?
- Which factors influence catalytic activity (why are some materials active and some not)?

2. Homogeneous catalytic ozonation

Homogeneous catalytic ozonation utilises ozone decomposition by transition metal ions. Two major mechanisms of homogeneous catalytic ozonation can be found in the published research papers:

1. Decomposition of ozone by metal ions leading to the generation of free radicals [13–15].
2. Complexes formation between organic molecule and the catalyst and subsequent oxidation of the complex [16–18].

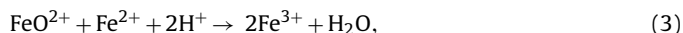
It has to be emphasised here that several parameters such as: pH of solution and concentration of the transition ion can influence both the efficiency of the process and its mechanism.

Several metal ions were found to be effective as catalysts of the ozonation process. Among the most widely used are: Mn(II), Fe(III), Fe(II), Co(II), Cu(II), Zn(II) and Cr(III) [18–20]. Fe(II)/O₃ and Fe(II)/O₃/UV processes are based on Fenton or photo-Fenton reactions [14,15,21]. Several homogeneous catalysts and studied organic contaminants are presented in Table 1.

Sauleda and Brillas [15] proposed the following reactions (based on earlier work by Logager et al. [22]) explaining the formation of hydroxyl radicals in the presence of Fe(II) ions:

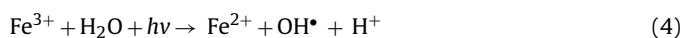


But because, at higher concentrations of Fe(II), FeO²⁺ can be oxidised to Fe(III) without the formation of radical intermediate species [15]:



reactions leading to radicals generation take place only at low concentrations of Fe(II). This is an important limitation of the process, which was discussed by Sauleda and Brillas [15] in work focusing on the catalytic ozonation of chlorophenol and aniline in water.

The results of a different study by Piera et al. [14] revealed that photochemical reduction of Fe³⁺ being formed is vital for the process to result in hydroxyl radicals' generation. In the presence of UVA light the following reaction takes place [14]:



Therefore oxidation/reduction reactions play an important role in catalytic ozonation systems utilising transition metals. Oxidation/reduction reactions characteristic for Fe(II)/O₃ were observed also for Mn(II) ions [13,21,23,24].

On the other hand, catalytic ozonation of oxalic acid in the presence of Co(II) ions was reported by Pines and Reckhow [16] to proceed via complex formation between an organic molecule and metal ion (Fig. 1). A similar mechanism was proposed for catalytic ozonation of oxalic acid in the presence of MnO₂ [25]. Pines and Reckhow [16] reported that high mineralization of oxalic acid takes place via ozonation in the presence of Co(II) ions. This process was characterised by a high reaction rate, which increased with a decrease of pH. This suggests that the oxidation reaction does not depend on the formation of hydroxyl radicals. The reaction rate was also found not to change in the presence of tert-butanol, a radical scavenger, which confirms the hypothesis that hydroxyl radicals are not responsible for mineralization of oxalate in the Co(II)/O₃ system [16].

Beltrán et al. [17] also confirmed that hydroxyl radicals are not responsible for the mineralization of oxalate in the Co(II)/O₃ system. In another paper, Beltrán et al. [18] revealed that Fe(III) ions also catalyse mineralization of oxalic acid and this process is not affected by the presence of tert-butanol. The following sequence of

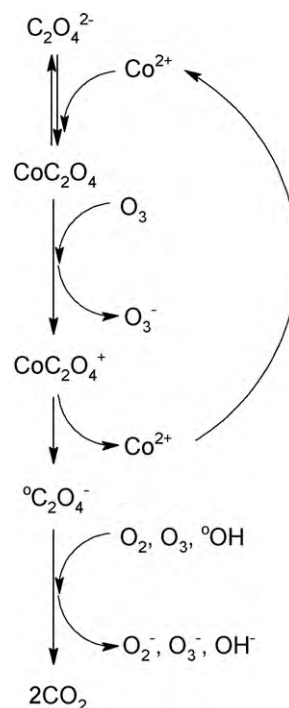
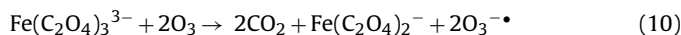
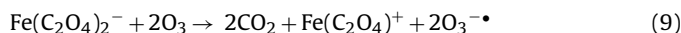
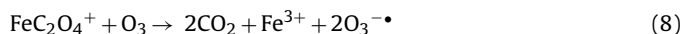
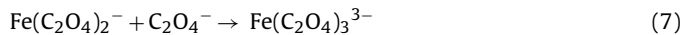
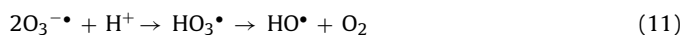


Fig. 1. Mechanism of oxalic acid oxidation in the presence of Co(II) ions proposed by Pines and Reckhow (modified from [16]).

reactions was proposed to explain the process [18]:



According to the above equations molecular ozone reacts with Fe-oxalic acid complexes, both with positively (reaction (8)) and negatively charged (reactions (9) and (10)) moieties. As a result both oxidation of oxalate ion to CO₂ and formation of O₃^{-•} take place. O₃^{-•} can be subsequently protonated and then undergo decomposition with the formation of hydroxyl radical and oxygen [18]:



It should, however, be emphasised here that the Fe(III) in the process of the decomposition of oxalic acid is under acidic conditions much less efficient when compared to Co(II) [16].

From the above discussion it can be therefore concluded that catalytic ozonation does not always proceed via free radicals reactions. Molecular ozone can also lead to high mineralization of organic matter if its reactions are catalysed by metal ions.

In the above mechanism proposed by Beltrán et al. [18] Fe ion does not play an 'active' part in the mineralization of oxalic acid. This is the major difference when Beltrán's mechanism is compared with the one proposed by Pine's and Reckhow [16], according to whom Co ion is initially oxidised from Co(II) to Co(III) and only the subsequent reduction of Co(III) allows for oxidation of oxalic acid.

Similarly, Andreozzi et al. observed higher efficiency of pyruvic acid ozonation in the presence of Mn(IV) [24]. The process was found to be pH dependent as its efficiency increased with a

decrease of pH. The effect of tert-butanol and sodium bicarbonate on catalytic ozonation indicates that the process proceeds via a radical chain reaction [26]. Additionally, in another paper by Ma and Graham [27] both Mn(II) and Mn(IV) were found to have similar activity. Furthermore, Xiao et al. [28,29] reported that Mn(II) reveals catalytic activity in the removal of dinitrotoluene (DNT) and the presence of oxalate plays a vital role in this activity. It has to be mentioned here that ozonation of DNT does not lead to the formation of oxalic acid as a by-product of the reaction. On the other hand, catalytic activity of Mn(II) ions was not observed in the presence of oxalate ions during the process of dichlorophenol ozonation, oxidation of which leads to the formation of oxalic acid. In other research by Pi et al. [19] no catalytic activity of Mn(II) ions in the process of oxalic acid removal at pH 7.5 was observed as opposed to Co(II), which revealed a high catalytic potential. According to Abd El-Raady and Nakajima [20] catalytic ozonation of carboxylic acids in the presence of Co(II) or Mn(II) is more efficient than O_2/H_2O_2 . Sánchez-Polo and Rivera-Utrilla [30] confirmed the high catalytic activity of Mn(II) and Fe(II) ions during ozonation of 1,3,6-naphthalenetrisulfonic acid and also were the first to prove catalytic activity of Zn(II). According to this group only those metals that can be oxidised by ozone and then undergo subsequent reduction are active [30]. Such a mechanism pathway is in accordance with the previously discussed work by Pines and Reckhow [16].

In contrast to the above discussion, Trapido et al. [31] did not observe catalytic activity in the case of Mn(II) during the process of dinitrobenzene ozonation. Similarly, Pi et al. [19] reported the lack of activity of Mn(II) ions in the ozonation of sulfosalicylic acid. It is surprising, as Mn(II) has been the subject of extensive research and its high activity was always observed [11].

Other metal ions were also found to reveal activity in catalytic ozonation of organic molecules. During ozonation of DNB the highest catalytic activity was observed in the presence of Fe(II) and Ni(II) ions [31]. Pi et al. [19] reported activity of Cu(II) ions during mineralization of oxalic acid at pH 7.5. A similar catalytic effect of Cu(II) was observed during ozonation of benzoic acid [24]. On the other hand Cu(II), as opposed to Co(II), did not reveal catalytic activity during ozonation of pyruvic acid in pure water [32].

Based on the results reported by some authors [16–18,24,27] it can be concluded that during homogeneous catalytic ozonation, initial complex formation between organic molecule and metal ion (Co(II), Mn(II) or Fe(II)) takes place and is followed by an attack of ozone molecule on the complex leading to the formation of hydroxyl radicals, which are responsible for further oxidation of organic matter.

From the above discussion, it can be observed that the mechanisms reported in the literature are contradictory. Homogeneous catalytic ozonation is not as popular as heterogeneous catalytic ozonation. As discussed above, not all the processes occurring are understood. Additionally, the application of homogeneous catalytic ozonation in water treatment would require the removal of metal ions from treated water, and therefore seems impractical (however, catalytic activity of Mn(II) ions could find applications). It is more likely that such processes might find applications in wastewater treatment. However, it should be emphasised that catalytic activity of metal ions is observed for low concentrations of several mg/L. It is also worth mentioning here that catalytic effects observed for metal ions are usually an initial stage of research leading to the introduction of heterogeneous catalysts [16,17,33,34].

3. Heterogeneous catalytic ozonation

Among the most widely used catalysts in heterogeneous catalytic ozonation are:

- Metal oxides (MnO_2 , TiO_2 , Al_2O_3 , $FeOOH$ and CeO_2).
- Metals (Cu, Ru, Pt, Co) on supports (SiO_2 , Al_2O_3 , TiO_2 , CeO_2 and activated carbon).
- Zeolites modified with metals.
- Activated carbon.

For a catalyst to reveal catalytic activity, adsorption of ozone and/or organic molecule on its surface has to take place. Adsorption of ozone in various gas–solid phase systems was widely reported [2]. It is however much more difficult to prove the adsorption of ozone on solid surfaces in an aqueous medium and therefore no comprehensive discussion has been published to date. All adsorptive centres of relevance to catalytic processes reveal high affinity towards water. Therefore adsorption of ozone would have to take place in the environment, where ozone molecules compete with water molecules. Water molecules are characterised by high polarity (dipole moment, 1.85D) as opposed to ozone (dipole moment, 0.46D), which reveals non-polar character despite its high polarizability. Furthermore, in the majority of published papers a rather low adsorption of organic molecules is observed. As a result, ozone decomposition on the surface of the catalysts is usually given as a factor determining activity of the catalyst. This is also because the high capacity of such catalytic systems to generate hydroxyl radicals is often observed. There are several mechanisms governing catalytic ozone decomposition proposed:

- Ozone decomposition on oxidised/reduced form of metal deposited on the surface of a solid support (a similar process to the one observed in the case of homogeneous catalytic ozonation; according to Pines and Reckhow [34] the success of catalytic activity lies in the capacity of the system to form a surface complex).
- Decomposition of ozone on Lewis centres of metal oxides (Al_2O_3 , TiO_2 , ZrO_2 , etc.). The likelihood of such reactions occurring is supported by the fact that a decrease of ozone decomposition is observed in the presence of phosphates or sulfates, which are known to have high affinity towards Lewis centres. Ozone adsorption and decomposition is observed in gas-metal oxide systems [35]. Unfortunately, there is no direct evidence of ozone adsorption on metal oxides in the presence of water. Roscoe and Abbatt [35] reported that there is competition between ozone and water for adsorption sites on alumina in the gaseous phase and that water molecules reveal much higher affinity towards alumina's surface sites than ozone, which results in the inability of ozone molecules to adsorb. The above will also concern other metal oxides.
- Ozone decomposition takes place on non-dissociated hydroxyl groups of metal oxides [36–38].
- Ozone decomposition of activated carbons takes place on basic centres of the catalyst [39,40].

It can be therefore concluded that all active sites are considered as potential catalytic centres responsible for ozone decomposition.

3.1. Metal oxides

Several metal oxides were studied as possible catalysts of the ozonation process. Among them are: MnO_2 , Al_2O_3 , TiO_2 and $FeOOH$ (Table 2). Advances in their possible application are briefly described below.

There are several factors that affect the heterogeneous catalytic ozonation process. Among the most important are: temperature and pH, which significantly influence ozone stability in water. Ozone decomposition constant is strongly pH dependant and increases with an increase of pH. The pH value also influences the properties of metal oxides' surfaces such as their charge, which has direct effect on the adsorption capacity of these metal oxides

Table 2
Heterogeneous catalytic ozonation – metal oxides.

Catalyst	Organic compound	Reference
MnO ₂	Carboxylic acids (oxalic, pyruvic, sulfosalicylic, propionic, glyoxalic) N-methyl-p-aminophenol, atrazine,	[16,17,19,27,30,42,164]
Al ₂ O ₃	Carboxylic acids (oxalic, acetic, salicylic, succinic), 2-chlorophenol, chloroethanol, NOM, dimethylphthalate	[46,50,51,164,174,175]
TiO ₂	Oxalic acid, carbamazepine, naproxen, nitrobenzene, clofibrilic acid	[78,81–83]
FeOOH	p-Chlorobenzoic acid, NOM	[37,59–61,63]
TiO ₂ , Al ₂ O ₃ , Ni ₂ O ₃ , CuO, MoO ₃ , CoO, Fe ₂ O ₃	m-Dinitrobenzene	[31]
ZnO	p-Chlorobenzoic acid	[25,86]
TiO ₂ (2.5%)/α-Al ₂ O ₃	NOM	[176–178]
TiO ₂ (10%)/Al ₂ O ₃ , Fe ₂ O ₃ (10%)/Al ₂ O ₃	Oxalic acid, chloroethanol, chlorophenol	[46]
TiO ₂ /Al ₂ O ₃	Fulvic acids	[179]
TiO ₂ (15%)/γ-Al ₂ O ₃	Oxalic acid	[52]
MnO ₂ (10%)/TiO ₂	Phenol	[18]
MnO _x (10.8%)/activated carbon	Nitrobenzene	[138]
β-Al ₂ O ₃	Pyruvic acid	[53]
γ-Al ₂ O ₃	Methylisoborneol	[54]
γ-Al ₂ O ₃ , γ-AlOOH, α-Al ₂ O ₃	2,4,6-trichloroanisole	[55]
MnO ₂	Phenol, NMO	[44,45]
CeO ₂	Aniline, sulfanilic acid, dyes	[43,66]
Co ₃ O ₄ /Al ₂ O ₃	Pyruvic acid	[53]
CuO/Al ₂ O ₃	Alachlor	[90]
CuO/Al ₂ O ₃	Oxalic acid	[19]
CuO/Al ₂ O ₃	Substituted phenols	[91]
Co(OH) ₂	p-Chloronitrobenzene	[69]
TiO ₂ /AC	Methylene blue	[84]
NiO/Al ₂ O ₃	Oxalic acid	[88]
NiO/CuO	Dichloroacetic acid	[92]
SnO ₂	Wastewater	[87]
MnO _x /Al ₂ O ₃	Phenazone, ibuprofen, phenytoin, diphenhydramine	[180]
MgO	Dye	[93]
CoO _x /ZrO ₂	2,4-D	[71]
Co/CeO, Ag/CeO, Mn/CeO	Phenolic wastewater	[94,95]

towards organic molecules. Detailed discussion on charge–pH relationship can be found in a review published earlier by the authors [11].

3.1.1. MnO₂

MnO₂ is the most widely studied metal oxide as a catalyst of the ozonation process. It is reported to be the most efficient in ozone decomposition in gaseous medium [2]. Its catalytic activity in aqueous medium is known to increase with a decrease of pH [24,25,41]. It has also been reported that commercial MnO₂ is not active, as opposed to MnO₂ formed *in situ* [41,42]. There is unfortunately a lack of understanding of the mechanisms governing catalytic reactions on MnO₂. According to Tong et al. [41] adsorption of organic molecule on the surface of MnO₂ and subsequent attack of ozone on adsorbed organic molecule are responsible for catalytic activity. Such a mechanism was initially proposed by Andreozzi et al. [25]. Catalytic activity of MnO₂ observed at pH 1 in the case of sulfosalicylic acid (pK_a, 2.85), and the lack of such activity in the case of propionic acid (pK_a = 4.86), seem to support such a hypothesis. Similarly, a lack of catalytic activity is observed for MnO₂ at pH of solution higher than its pHPZC [30].

MnO₂, cobalt and cerium oxides were also verified as catalysts of ozonation of aniline and sulfanilic acid. However, the highest efficiency was reported in the case of mixtures of metal oxides such as Ce–Mn and Co–Ce catalysts [43]. In other work, the activity of several metal oxides in m-dinitrobenzene ozonation at pH 3 was observed to increase in the following order: ozone ≈ MnO₂ ≈ Cr₂O₃ < TiO₂ < Al₂O₃ < Ni₂O₃ ≈ CuO < MoO₃ < CoO < Fe₂O₃. MnO₂ therefore did not reveal catalytic activity in the removal of m-dinitrobenzene. In the same study, better results were observed for higher ozone doses. It was also reported that V₂O₅ leads to an inhibition of oxidation of m-dinitrobenzene [31]. Furthermore, Dong et al. [44] reported the high activity of β-MnO₂ nanowires during the removal of phenol, with only a very low

(8%) adsorption of phenol on β-MnO₂ observed. Twice as high efficiency of phenol removal was observed in the case of catalytic ozonation (after 30 min ozonation time) when compared to ozonation alone. Decomposition of ozone was also more significant, which indicates radical reactions occurring. Furthermore, it was observed that Mn ions dissolving into the solution negatively impact the efficiency of the catalytic process [44]. However, it has to be emphasised here that a high catalyst dose (160 mg) was used in order to oxidise 16 mg of phenol. In another work, catalytic ozonation in the presence of MnO₂ was found to effectively remove TOC and COD [45].

3.1.2. Al₂O₃

Al₂O₃ is another metal oxide that has been studied as a catalyst in the catalytic ozonation of organic contaminants. According to Oyama [2] decomposition of ozone in gaseous phase takes place on semiconductor catalysts (both type “n” and “p”). The highest activity is observed for semiconductor catalysts of ‘p’ type such as: MnO₂, NiO, Co₃O₄ and Fe₂O₃. Al₂O₃ has not been placed among these active catalysts by Oyama [2] and so far it has been used more as a catalyst's support (for another metal oxide or metal) rather than an actual active material with catalytic properties. However, Cooper and Burch [46] reported that ozone decomposition takes place on the surface of Al₂O₃, as a result increasing the efficiency of oxalic acid, chloroethanol and chlorophenol degradation. Unfortunately, lack of control of pH in this work and no adsorption studies undertaken make interpretation of the results from a mechanistic point of view impossible. Kasprzyk-Hordern and Nawrocki [47,48] reported no catalytic activity of Al₂O₃ during the removal of aromatic hydrocarbons [47]. No removal of ethers was also observed in the presence of Al₂O₃ [49]. In the same work, alumina, despite revealing no activity in the removal of ethers, was found to cause twice as high ozone decomposition than ozonation alone [49]. As both hydrocarbons and ethers do not adsorb on alumina from aque-

ous solutions it might be suggested that adsorption of organics is an important stage of the effective catalytic process on Al_2O_3 . Furthermore, Kasprzyk-Hordern et al. [50] demonstrated the high efficiency of NOM removal during its ozonation in the presence of alumina. In this case, alumina revealed high adsorption capacity towards NOM. Catalytic ozonation resulted in twice as high efficiency when compared to ozonation alone. During 62 cycles of the catalytic process, each 3 h long, no significant decrease of degradation efficiency was observed. The difference between catalytic activity of alumina in the removal of aromatic hydrocarbons/ethers and NOM might therefore result from the different adsorption capacity of alumina towards aromatic hydrocarbons and NOM. In contrast to these findings, Ernst et al. [51] reported that adsorption of organic molecule is detrimental to catalytic activity of $\gamma\text{-Al}_2\text{O}_3$. Several model compounds (oxalic, acetic and succinic acids) were studied by Ernst et al. [51]. The best results were observed for succinic acid, a compound that was adsorbed to $\gamma\text{-Al}_2\text{O}_3$ to a limited extent. Oxalic acid, on the other hand, revealed much higher adsorption affinity towards alumina, which resulted in a decrease of catalytic ozonation efficiency. Beltrán et al. [52] observed similar results during the process of catalytic ozonation of oxalic acid at pH 2.5 in the presence of alumina. It was also reported that the presence of phosphate buffer decreases the catalytic activity of alumina. Álvarez et al. [53] additionally reported that adsorption of ions of phosphate buffer on the surface of alumina is competitive against pyruvic acid ions and significantly decreases their adsorption [53]. This group also observed that adsorption of pyruvic acid on the surface of alumina is a necessary step of the catalytic ozonation process as oxidation reactions take place for the acid's molecules already adsorbed on the surface of the catalyst [53]. These findings are contradictory to those discussed above [51].

In a different paper, Chen et al. [54] revealed high efficiency of $\gamma\text{-Al}_2\text{O}_3$ as a catalyst of 2-methylisoborneol ozonation. The highest activity of the catalyst was observed at pH of solution close to pH_{PZC} , which indicates that neutral (uncharged) surface of the catalyst is responsible for hydroxyl radicals generation. Another chemical, 2,4,6-trichloroanisole, was also found to be effectively removed on aluminium oxides ($\gamma\text{-AlOOH}$, $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$). The higher density of surface hydroxyls and stronger surface Brønsted acidity enhanced catalytic activity of aluminium oxides [55]. The influence of surface properties of alumina on its ability to decompose ozone was studied by Qi et al. [56]. It was reported that the highest activity of alumina takes place at $\text{pH} = \text{pH}_{\text{PZC}}$, which indicates that ozone decomposition occurs on non-charged surface hydroxyl groups. Qi et al. [56] also observed that the higher number of hydroxyl groups on the surface of alumina, the higher the activity of the catalyst. Unfortunately, measurements of the number of hydroxyls present on the surface of alumina were undertaken with a not very reliable method and with the sample dried at temperature of 70 °C, which is too low to remove adsorbed water. The above hypothesis indicating the importance of surface hydroxyls in catalytic activity of alumina is supported by the fact that nitrates and sulfates inhibit the activity of alumina due to adsorption on its surface (via substitution of surface hydroxyls). It has to be emphasised here that the ion-exchange capacity of alumina will be relatively low at $\text{pH} = \text{pH}_{\text{PZC}}$ [56]. However, in the above reports it has not been proven that ozone decomposition occurs on the surface of alumina.

On the other hand, Lin et al. [57] reported that ozone in aqueous solutions is not decomposed by alumina which is contradictory to all the above cited published work, but it supports results published by Pines and Reckhow [34] and Kasprzyk-Hordern et al. [50].

The above discussion indicates that contradictory results are published in literature. This suggests the necessity for a greater standardisation of research concerning catalytic activity of new catalysts. The most urgent matter concerns the phenomenon of ozone

decomposition in the presence of metal oxides. It has to be therefore verified whether ozone is decomposed on the surface of the catalyst leading to the formation of hydroxyl radicals or whether such radicals are formed as a result of reaction with adsorbed organic molecules. The second hypothesis seems to be supported by the results published by Kasprzyk-Hordern et al. [50] or Álvarez et al. [53]. The other matter concerns the role of the organic molecule. It is suggested that its structure and resulting capacity to adsorb on the surface of alumina plays a vital role in the catalytic ozonation process and mechanisms implemented.

3.1.3. Fe, Ce and Co oxides

Another catalyst that has received significant attention is FeOOH. Granulated forms of iron oxide are already used in water treatment technology as sorbents for the removal of As(V) [58]. Park et al. [59,60] reported the usage of commercially available goethite in the removal of natural organic matter. It was observed that FeOOH initiated ozone decomposition and subsequent hydroxyl radical formation. The observed catalytic effect was not significant at pH 7 but a higher mineralization of organic matter was noted. It was suggested that negatively charged surface groups Fe-O_2^- that are formed as a result of dissociation of surface hydroxyl groups have a major effect on ozone decomposition. As pH_{PZC} of studied goethite was 7.8, higher decomposition of ozone was observed at basic pH. Furthermore, it was also reported that at pH 2 degradation of p-chlorobenzoic acid (p-CBA) was independent on the presence of tert-butanol, which suggested that a reaction with hydroxyl radicals takes place on the surface of the catalyst and not in bulk solution. However, the authors indicated that only a small percentage of p-CBA is ionised at pH 2 and capable of adsorption on the surface of the catalyst. It was therefore suggested that degradation of p-CBA takes place on the surface of the catalyst at $\text{pH} < 3$. At higher pH values the majority of p-CBA is degraded in the solid-liquid interface [61].

Beltrán et al. [18] studied catalytic ozonation of oxalic acid on $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. They found out, similarly to Park et al. [61], that the removal of oxalate is independent of the presence of tert-butanol. Therefore it was suggested that the mechanism of reaction does not involve hydroxyl radicals generation but it proceeds via the reaction of molecular ozone in bulk solution and surface complex between Fe and oxalic acid. It is worth mentioning that Park et al. [59–61] used very high doses of the catalyst in relation to the concentration of ozonated organic compound. Zhang and Ma [62] also studied goethite as a possible catalyst of the ozonation process. They reported catalytic activity of goethite in the removal of nitrobenzene. It was found that nitrobenzene does not adsorb on the surface of the catalyst and despite this fact catalytic ozonation results in three times higher efficiency when compared with ozonation alone. No decrease of catalytic activity of the catalyst was observed after several processes had been undertaken. The catalytic ozonation process was found to proceed via a radical pathway. The suggested mechanism included ozone decomposition on hydroxyl groups present on the surface of FeOOH leading to hydroxyl radicals generation (Fig. 2). However, the authors of this review think that this mechanism is rather unlikely. According to the suggested mechanism the ozone molecule forms a ring with hydroxyl group, which decomposes with the formation of oxygen and $\text{Fe-OH(O}^\bullet\text{)}$ group. $\text{Fe-OH(O}^\bullet\text{)}$ subsequently reacts with water leading to the formation of $\text{O}_2^{\bullet-}$ and hydroxyl radical. In our opinion, such a reaction is rather doubtful as it would lead to the breakage of a strong bond between Fe and oxygen. It has to be remembered that the hydroxyl group is usually strongly hydrated with water molecules.

According to Zhang and Ma [62] the generation of hydroxyl radicals takes place on neutral surface hydroxyl groups. They tried to prove such hypothesis for different metal oxides. It has to be

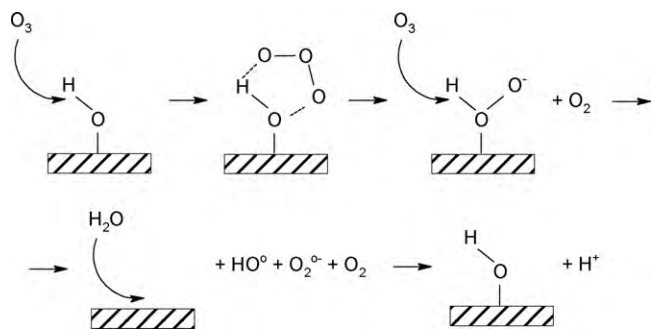


Fig. 2. Mechanism of hydroxyl radicals generation in the presence of FeOOH (modified from [62]).

however emphasised that in their work no direct influence of the catalyst on the stability of ozone in water was presented (in contrast Park et al. [61] demonstrated the influence of goethite on the stability of ozone). In another paper, the same research group led by Ma studied the catalytic activity of several iron oxides during ozonation of nitrobenzene [36]. They reported that anions such as phosphates and sulfates decrease catalytic activity of iron oxides, which, according to the authors, results from a decrease in the concentration of surface hydroxyl groups. It was also suggested that not all hydroxyl groups are catalytically active [36]. The influence of anions commonly present in natural waters should therefore be one of the most important parameters included in the assessment of the catalytic activity of the studied materials. It should be remembered that anions such as phosphates are strong Lewis bases and their influence on the decrease of catalytic activity of metal oxides could be simply an indication of how important Lewis centres are in catalytic processes occurring during catalytic ozonation.

Sui et al. [94] investigated catalytic ozonation of oxalic acid in the presence of FeOOH and observed that FeOOH can effectively promote the generation of hydroxyl radicals under acidic and neutral pH conditions, which resulted in the enhancement of the removal of oxalic acid by ozone. It was suggested that both neutral ($\text{Me}-\text{OH}$) and positively charged ($\text{Me}-\text{OH}_2^+$) surface groups are responsible for ozone decomposition and hydroxyl radicals generation. Adsorption of oxalate was found to take place on the surface of FeOOH. It was also observed that the ligand exchange of surface hydroxyl groups by phosphate ions decreased the adsorption of oxalate ions on FeOOH and the catalytic activity of FeOOH. In contrast, phosphate was found to desorb from the surface of FeOOH in the presence of ozone, resulting in the reactivation of the catalytic activity of FeOOH. Sui et al. [94] therefore suggested that ozone is a stronger Lewis base than phosphates. Furthermore, they concluded that catalytic activity of metal (hydr)oxides depends on the presence of Lewis bases and their strength when compared to ozone. This statement has important implications as far as mechanisms of catalytic ozonation on metal oxides are concerned.

In another paper, Zhang et al. [37] studied the effect catalytic ozonation on goethite can have on certain fractions of NOM. The results obtained were compared with another set of results collected for cerium oxide [37,63]. Iron oxides deposited on several metal oxides were obtained via impregnation and calcination of supports with Fe salts [64]. The highest activity in the process of catalytic ozonation of humic acids was observed in the case of iron oxide deposited on MgO. Unfortunately, in this work no control of pH was undertaken and therefore it is highly likely that the observed effects were simply a result of an increase of pH due to the presence of MgO. Catalytic ozonation on FeOOH and CeO_2 can also be utilised in order to decrease the potential of the formation of bromate [65]. Cerium oxide was found to be particularly effective. This aspect of catalytic ozonation has never been studied in detail

before. CeO_2 also showed high catalytic activity in the ozonation of aniline, sulfanilic acid [43] and dyes [66]. Cerium oxides were also found to be effective in the ozonation of simulated wastewater containing phenolic compounds [67]. Succinic acid ozonation on cerium oxide, which was characterised by a high surface area ($\sim 200 \text{ m}^2/\text{g}$) and resulted in an adsorption of acid, was found to be an effective process. However, cerium oxide of a much lower surface area of $\sim 40 \text{ m}^2/\text{g}$ did not provide such efficiency [68].

Cobalt hydroxide was found to be an effective catalyst of p-chloronitrobenzene ozonation at pH 7.5 [69]. It was observed that cobalt hydroxide enhances ozone decomposition in water. Unfortunately a decrease of its activity was observed with every additional ozonation cycle. Additionally, cobalt underwent dissolution in water to some extent but it was shown that Co present in bulk solution is not responsible for catalytic effect [69]. CoO , CoAl_2O_4 and $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ were studied as possible catalysts of pyruvic acid ozonation. $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ was the most effective under acidic pH [53]. $\text{Co}_2\text{O}_3/\text{Al}_2\text{O}_3$ was also found to cause effective ozone decomposition. Furthermore, ozone decomposition was observed to be even more rapid in the presence of the catalyst and tert-butanol [70].

$\text{CoO}_x/\text{mesoporous zirconia}$ was also found to be an effective catalyst for the ozonation of 2,4-D [71]. It was observed that the multivalence oxidation states and high dispersion of CoO_x enhanced the interfacial electron transfer, causing higher catalytic reactivity. Formation of hydroxyl radicals resulting from the catalytic decomposition of ozone was found to be the reason for accelerated removal of 2,4-D from the aqueous solution. The highest efficiency of the process was observed at basic pH $> \text{pH}_{\text{PZC}} = 5.5$, which is when the surface of the catalyst was negatively charged. Under these conditions adsorption of dissociated 2,4-D was found to be negligible.

3.1.4. TiO_2

Titania is mainly used as a photocatalyst [72–77]. Beltrán et al. [78] showed that TiO_2 can be also used as an active catalyst in the ozonation of organic molecules such as oxalic acid. The authors suggested that both ozone and oxalic acids are adsorbed at pH 2.5 (similarly to gas phase reactions) on the surface of the catalyst, followed by a subsequent reaction between the two moieties. Unfortunately, in the literature there is no direct proof of ozone adsorption on metal oxides in the presence of water. In another paper, Addamo et al. [79] reported photocatalytic oxidation to be very effective at pH 10 in the removal of oxalic acid in water in the presence of oxygen. On the other hand, Yang et al. [38] studied ozonation of nitrobenzene on nano- TiO_2 and observed that nano- TiO_2 is catalytically active if present in the form of rutile and not anatase. Adsorption of nitrobenzene was found to play an important role and degradation of this compound proceeded via a radical pathway. According to the authors radicals are formed on the hydroxylated surface of nano- TiO_2 , and the process is especially effective at a pH close to pH_{PZC} , which indicates that neutral hydroxyls are responsible for the formation of hydroxyl radicals. Earlier work [34] showed no ozone decomposition on anatase- TiO_2 at a pH close to its pH_{PZC} . Ye et al. [80] studied the degradation of 4-chloronitrobenzene (CNB) during catalytic and photocatalytic ozonation in the presence of TiO_2 . Both photocatalytic and catalytic processes revealed similar efficiency of the decomposition of CNB, but photocatalysis resulted in higher mineralization of CNB [80]. Catalytic activity of TiO_2 was also investigated in the process of the removal of pharmaceuticals such as carbamazepine and naproxen [81]. TiO_2 had an effect on the mineralization of ozonation by-products and their composition. It was observed that in the presence of the catalyst the generation of hydroxyl radicals takes place at pH 5. On the other hand, at a neutral pH, the inhibition of hydroxyl radicals formation was noted in the presence of TiO_2 .

Table 3
Heterogeneous catalytic ozonation – metals on supports.

Catalyst	Organic compound	Reference
Pt, Pb, Pd, Ag, Co, Ru, Ir, Rh, Re/Al ₂ O ₃ , SiO ₂ , activated carbon	Formic acid	[181]
Cu(10 wt%)/Al ₂ O ₃ , Cu(5 wt%)/TiO ₂ , Cu(5 wt%)/clay	Humic substances, salicylic acid, peptides	[182]
V-O/TiO ₂ , V-O/SiO ₂	Sulfosalicylic acid	[183]
Ru(2%)/CeO ₂	Succinic acid	[68,98]
Ru(2%)/CeO ₂ -TiO ₂	Chloroacetic and succinic acid	[96]
Ru(5%)/Al ₂ O ₃ , Pt(5%)/Al ₂ O ₃ , Pt(5%)/AC	p-Chlorobenzoic acid	[34]
Ru(0.1%)/Al ₂ O ₃	Dimethyl phthalate	[174]
Cu-ZrO ₂ /Al ₂ O ₃ , Ru-CeO ₂ /TiO ₂	Pyruvic acid, succinic acid	[97]
Rh-CeO ₂	Pyruvic acid	[32]

Rosal et al. [82,83] studied the degradation of clofibric acid by means of catalytic ozonation on titania. It was suggested that the adsorption and subsequent reaction of organics on catalyst sites are responsible for the enhancement of ozonation rate observed in catalytic runs. The enhancement was however suggested not to result from a greater production of surface hydroxyl radicals from ozone. Both facts suggest that even if the catalytic surface plays a significant role in the production of hydroxyl radicals, the interaction of surface sites and organics is probably limited.

TiO₂ deposited on activated carbon was also found to be effective in the removal of methylene blue in the catalytic ozonation process. Higher efficiency of TiO₂/AC/O₃ process was observed when compared to AC/O₃ and was hypothesised as being due to the suspected acceleration of the formation of OH• radicals and adsorption of methylene blue on AC [84]. Unfortunately, no adsorption capacity of the catalyst was assessed and therefore the resulting high efficiency of the process might be simply a sum of two separate processes occurring: ozonation and adsorption.

3.1.5. Other metal oxides

Several other metal oxides were also studied as catalysts of the ozonation process. Among them are: ZnO [85,86] and SnO₂ [87]. Avramescu et al. [88] used NiO deposited on alumina as a catalyst of ozonation of oxalic acid and observed a high activity for the catalyst calcined at 550 °C. Other catalysts calcined at higher temperatures did not demonstrate high catalytic activity. The mechanism of radicals formation presented by Avramescu et al. [88] was based on mechanisms occurring in gas phase (for example presented in paper [2]). In another paper, Ni, V and Pd oxides were deposited on γ-Al₂O₃ also as a result of calcination in the air or nitrogen [89]. Their activity was studied in the process of hexadecane ozonation. It was suggested that hydrocarbon undergoes adsorption on the surface of the catalyst and is attacked by an ozone molecule from the bulk solution. The main product of the process was a mixture of ketones [89]. Copper oxide deposited on alumina was found to significantly increase mineralization of alachlor [90]. The same catalyst also showed catalytic activity during ozonation of oxalic acid at pH 3 [19] and substituted phenols [91].

According to Pines and Reckhow [34] metal oxides do not cause ozone decomposition in pure water leading to the formation of hydroxyl radicals. However, the presence of natural organic matter can lead to the formation of hydroxyl radicals, which is probably connected with the reaction of ozone molecule with organic molecule already adsorbed on the surface of the catalyst. However, some metal oxides with their surface modified with metals such as Ru/Al₂O₃ and Pt/Al₂O₃ are capable of ozone decomposition in water [34].

NiO/CuO was found to be effective in the ozonation of dichloroacetic acid despite negligible adsorption of this compound on the surface of catalyst [92]. It was suggested that the introduction of NiO/CuO nanoparticles can lead to violent interaction between ozone and the catalyst surface, hence promoting the decomposition of ozone and the generation of HO• radicals (gen-

eration of which was confirmed by the authors with EPR and DFT calculations) which, in turn, might lead to an increase in their catalytic ozonation efficiency. The formed HO• radicals act as promoters of chain reaction in the solution leading to the decomposition of ozone and further formation of HO• radicals in the solution.

MgO nanocrystals were demonstrated to be effective catalysts in the catalytic ozonation of dye-containing solution since they notably accelerated decolorization and COD removal. It was suggested that an increase of ozonation efficiency was due to the decomposition of ozone by MgO monocrystals leading to an accelerated formation of oxidative radicals [93]. Unfortunately, it is not clear whether pH of solution was measured before or after the introduction of MgO.

Martins and Quinta-Ferreira [67,95] also studied the mechanism of catalytic ozonation of phenolic wastewater in the presence of manganese oxide deposited on CeO catalyst. It was observed that pH and adsorption of organics on the surface of catalyst play a vital role in the catalytic process: the organic compounds were better catalytically degraded at low pH in contrast to single ozonation. It is well known that the solution pH determines the surface properties of the catalyst and ionisation of organics. As the pH_{PZC} for studied catalyst was 4.8, at a higher pH the catalyst will be negatively charged as well as the phenolic and carboxylic acids (with a pK_a around 4.0–4.5), creating repulsive electrostatic interactions between the catalyst and pollutants that will inhibit the surface reactions. Additionally the presence of radical scavengers (t-butanol, carbonate) did not influence the efficiency of the process, which indicates that the catalyst did not promote ozone decomposition to hydroxyl radicals. It was therefore proposed that the catalytic degradation of the phenolic acids by ozone may mainly follow a mechanism of surface reactions involving the adsorption of both ozone and pollutants.

3.2. Metals on supports

Among metals on supports used as catalysts of ozonation are: ruthenium or copper deposited on supports such as ZrO₂/Al₂O₃, CeO₂, CeO₂/TiO₂ or Al₂O₃. Table 3 presents types of catalysts and organic molecules studied in the process of catalytic ozonation.

The application of ruthenium deposited on several supports as a possible catalyst of ozonation was discussed in several papers [34,68,96,97]. Karpel Vel Leitner et al. [68] reported that the method of catalyst preparation plays a vital role in its catalytic activity. Ruthenium deposited on a support via impregnation was found to be much more efficient than ruthenium deposited via ion exchange and revealed high efficiency in the decomposition of succinic acid in water, and additionally resulted in high mineralization of organic matter [68]. Carbajo et al. [32] reported high catalytic activity of Rh/CeO₂ during ozonation of pyruvic acid in water. Fu et al. [96] showed the importance of adsorption of organic molecule on Ru deposited on CeO₂/TiO₂. Karpel Vel Leitner et al. [97] studied the relation between catalytic activity of Ru–CeO₂/TiO₂ and pH of solu-

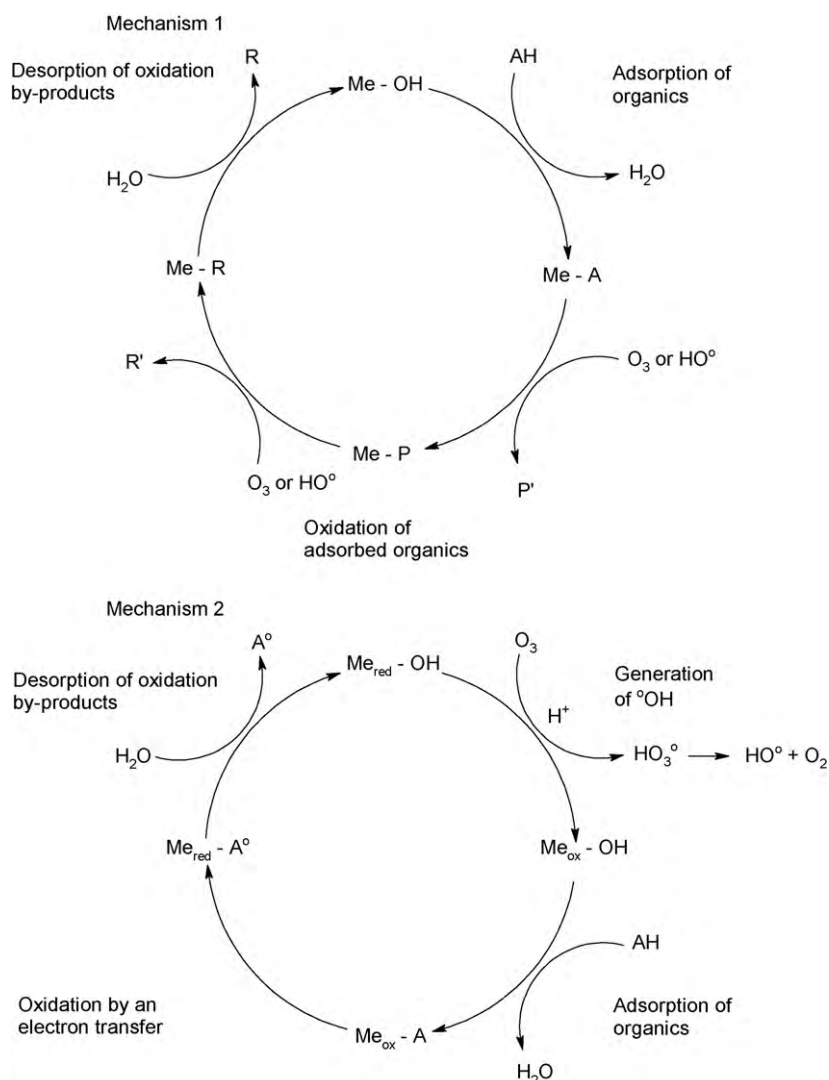
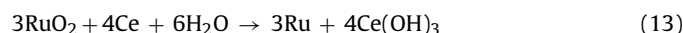


Fig. 3. Mechanisms of catalytic ozonation in the presence of metals on supports (AH – organic acid; P, R – adsorbed primary and final by-products; P', R' – primary and final by-products in solution respectively; modified from [9]).

tion. The highest catalytic effect during mineralization of succinic acid was observed at pH 3.6 with a reduced usage of ozone.

Catalytic activity in the process of the removal of pyruvic acid was also observed in the case of Cu–ZrO₂/Al₂O₃ [97]. Unfortunately in these works [68,96,97] no proof of the role of metal deposited on support in its reduced form was provided. However it was reported that adsorption of organic molecule plays an important role in the catalytic ozonation process, which might suggest that the presence of metal is not as vital. Delanoë et al. [98] on the other hand sug-

gested that the proximity of Ru and Ce is necessary for a redox reaction to occur:



Fonatnier et al. [99] published in 2005 a very significant paper in the field of catalytic ozonation. Unfortunately, apart from the type of the catalyst, no information on its composition was given. Sev-

Table 4
Heterogeneous catalytic ozonation – minerals.

Catalyst	Organic compound	Reference
Ceramic honeycomb	Nitrobenzene	[100–103]
Mn, Cu, K/ceramic honeycomb	Nitrobenzene	[104,108]
Mn, Fe, K/ceramic honeycomb	Benzophenone	[105]
Cu/cordierite	Nitrobenzene	[106]
Mn/ceramic honeycomb	Nitrobenzene	[107]
Fe, Ni, Zn/ceramic honeycomb	Nitrobenzene	[109]
Perovskite	Pyruvic acid, gallic acid, phenolic compounds	[111–114]
Zeolites	Phenol	[115]
De-aluminated Y zeolite	Phenol	[116]
Brucite, magnesia	Phenol	[119]
Bauxite	2,4,6-Trichloroanisole	[120]

eral organic compounds were studied and therefore mechanisms of ozonation of many organics could be provided. A significant increase of catalytic ozonation efficiency was observed in the case of carboxylic acids, chlorinated organic chemicals, sugars, phenols and several other compounds. Mineralization of organic carbon was 12–32 times higher than mineralization obtained via ozonation alone. The suggested mechanism indicated the formation of a highly reactive complex between metal and ozone molecule, which reacts with organic molecules present in bulk solution.

In summary, mechanisms of heterogeneous catalytic ozonation in the presence of metals on support (similarly to homogeneous catalytic ozonation in the presence of metal ions) differ from those observed in the case of heterogeneous catalytic ozonation on metal oxides. This is because no generation of free hydroxyl radicals is observed in the case of heterogeneous process in the presence of metals on supports. Instead, reactions on the surface of the catalyst or complexes formation are believed to be responsible for catalytic effects.

Possible mechanisms of catalytic ozonation in the presence of metals on supports are presented in Fig. 3 [9]. In the first mechanism organics adsorb on the surface of the catalyst and are attacked by ozone (or hydroxyl radicals) from bulk solution to give oxidation products, which desorb into bulk solution. In the second mechanism, both ozone and organic molecules adsorb on the surface of the catalyst. On the surface of reduced Me-catalyst (Mred) ozone oxidises metal with the generation of OH radicals. Organic molecules (AH) after adsorption on the catalyst surface are subsequently oxidised by an electron-transfer reaction to give again a reduced catalyst (MredA[•]). The organic radical species A[•] are subsequently desorbed from the catalyst and oxidized by HO[•] or O₃ either in bulk solution, or more probably, within the thickness of an electric double layer [9].

3.3. Minerals

Among minerals used as catalysts in ozonation processes are: cordierite, perovskite and zeolites, pure or modified with metals or metal oxides (Table 4).

Ceramic honeycomb (2MgO–2Al₂O₃–5SiO₂) of a low surface area denoting <0.5 m²/g was reported by Zhao et al. [100,101] to be an active catalyst of nitrobenzene ozonation. The process was found to proceed via a radical pathway [100,101] and the highest efficiency of the process was observed at pH of solution close to pH_{PZC} of the catalyst. Therefore it was suggested that surface bound hydroxyl groups are responsible for the formation of hydroxyl radicals. Furthermore, the authors identified products formed as a result of catalytic ozonation of nitrobenzene [100,101]. In other work, Zhao et al. [102] proved again that hydroxyl groups are responsible for the catalytic activity of ceramic honeycomb. The effect of temperature on catalytic activity of ceramic honeycomb was also studied [103]. The results indicated an increase of the degradation efficiency and mineralization as well as an increase of hydroxyl radicals formation with an increase of temperature from 278 K to 328 K [103]. Furthermore, the modification of ceramic honeycomb with Mn, Cu and K ions was found to additionally increase catalytic activity of the catalyst in the ozonation of nitrobenzene [104]. It was observed that modification of the surface of honeycomb with Mn, Cu and K results in a significant increase of its surface area from 0.35 m²/g to values as high as 4.37 m²/g and ability to initiate hydroxyl radicals generation. It is worth emphasising here that adsorption of nitrobenzene on the surface of the catalysts was negligible [104]. Benzophenone was found to be effectively removed via catalytic ozonation on honeycomb modified with Mn and Fe [105]. The highest efficiency of the process was observed at Mn:Fe ratio denoting 1:4. Additionally, it was reported that catalytic activity of honeycomb

did not decrease even after several ozonation cycles. Zhao et al. [106] also reported that cordierite modified with copper oxide revealed higher catalytic activity than unmodified cordierite during ozonation of nitrobenzene. Adsorption of nitrobenzene on both catalysts was minimal. The degradation efficiency of nitrobenzene was found to significantly increase with the loading percentage of Cu from 0 to 3%, while a further increase of Cu load resulted in a decrease of degradation efficiency. It was additionally observed that the highest generation of hydroxyl radicals also took place at 3% Cu and decreased with higher Cu loads. Zhao et al. [106] therefore suggested that a high concentration of Cu on the surface of the catalyst can cause a blockage of surface active sites (surface hydroxyls) of cordierite and result in a decrease of activity of the catalyst. The role of pH value of solution and pH_{PZC} of the catalyst was emphasised as an additional factor affecting the charge properties of surface hydroxyl groups and the resulting activity of the Cu modified catalyst [106]. The same group also studied the efficiency of the removal of nitrobenzene via ozonation on ceramic honeycomb impregnated with Mn salts [107]. Honeycomb impregnated with manganese nitrate and calcined at 723 K revealed much higher activity than unmodified honeycomb [107]. Similarly to the catalyst studied in [106], impregnation of cordierite with Mn resulted in a significant increase of surface area of the catalyst and increased the value of its pH_{PZC}. Only very limited adsorption of nitrobenzene was observed. However, in contrast to Cu-cordierite, the activity of Mn-cordierite increased with an increase of Mn loading to as high as 4%. This phenomenon was explained by the fact that the increase of loading percentage of Mn can lead to an increase of density of surface hydroxyl groups at neutral state as a result of a change (increase) of pH_{PZC} of the modified catalyst [107]. Similarly, in other work by the same research group [108], the modification of ceramic honeycomb by loading Mn and Cu resulted in a change of surface characteristics, such as the formation of MnO₂ and CuO crystalline phases, an increase of surface area and an increase in the density of surface hydroxyl groups responsible for the initiation of hydroxyl radicals' formation. It was suggested that Mn is the main active component of the catalytic system responsible for an increase of activity of modified ceramic honeycomb [108]. Zhao et al. [109] also studied honeycomb modified with other metals: Fe, Ni and Zn. Similarly to the work by Zhao et al. [107,109] discussed above, the modification of honeycomb with metals resulted in an increase of activity of the catalyst during ozonation of nitrophenol. Out of the three studied catalysts Fe-ceramic honeycomb revealed the highest activity in the degradation of nitrophenol and overall mineralization. Furthermore, the activity of the modified catalyst was found to be proportional to the loading percentage (studied range; 0–8%) of metal.

The mechanism proposed by Zhao et al. [108] for ozone decomposition on ceramic honeycomb impregnated with Mn and Cu is presented in Fig. 4. Uncharged surface bound hydroxyl groups cause ozone decomposition and the generation of intermediate species on the surface of the catalyst yielding the acceleration of nitrobenzene decomposition in bulk solution [108].

The same group suggested another mechanism for ozone decomposition on ceramic honeycomb modified with the following metals: Zn, Ni and Fe (Fig. 5) [109]. In this mechanism surface bound OH₂⁺ groups, and not neutral hydroxyls, are suggested to be responsible for catalytic activity. These groups interact with ozone with the formation of –HO[•] (steps 3–6), which is subsequently attacked by a water molecule resulting in a formation of a free hydroxyl radical. However, the authors of this review are sceptical as far as pathway 8 is concerned. It is proposed that the elimination of HO₃[•] and HO₄[•] from the surface of the catalyst leads to the formation of the surface cation, which can adsorb water molecule resulting in the formation of surface hydration cation (step 9) and

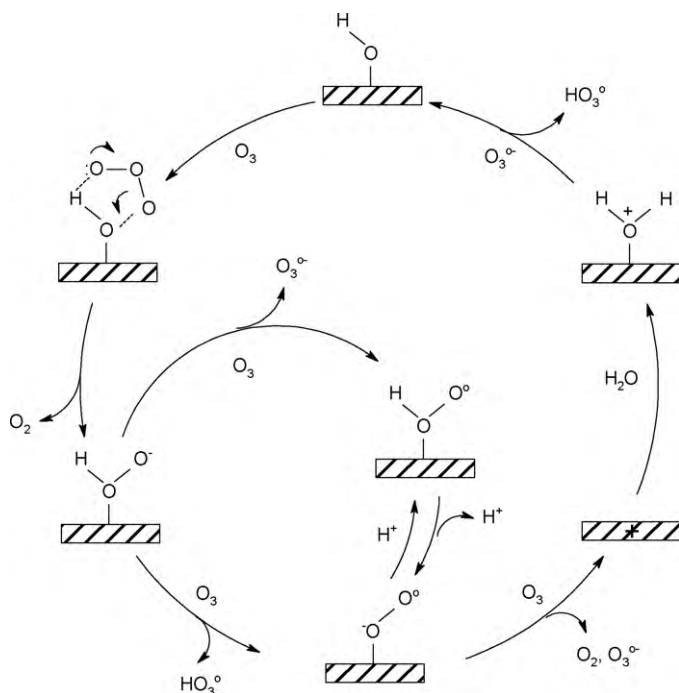


Fig. 4. Mechanism of ozone decomposition on the surface of ceramic honeycomb modified with metals (modified from [108]).

finally $-\text{OH}_2^+$ group. The breaking of metal–oxygen bond seems to be rather unlikely.

Azrague et al. [110] reported that ceramic material, which is used to produce Raschig's rings, is capable of ozone decomposition and hydroxyl radicals formation.

Another mineral used as a catalyst for ozonation is perovskite. Perovskites constitute a group of inorganic compounds of general formula ABX_3 , where A indicates a cation of metal from the group of alkali metals and beryllium, magnesium and alkaline earth metals, B is a cation of the coordination number of 6 (frequently titanium, niobium, tantalum and manganese) and X is an anion oxide O^{2-} , less frequently halide or sulfide ions. The name of the group originates from the mineral perovskite CaTiO_3 . In this group of minerals, $\text{LaTi}_{1-x}\text{Cu}_x\text{O}_3$ has attracted attention as a possible catalyst of ozonation in aqueous solutions. It was initially investigated as a catalyst for the oxidation of phenols with hydrogen peroxide. High catalytic activity resulting in a high mineralization of studied substances was observed [111]. Its activity is based on the generation of hydroxyl radicals, and its main disadvantage is dissolution of Cu^{2+} into bulk solution. Another perovskite represented by the formula $\text{LaTi}_{0.15}\text{Cu}_{0.85}\text{O}_3$ was studied as a catalyst for the removal of pyruvic acid at pH 2.5, which is when pyruvic acid does not react with ozone [112]. It was observed that tert-butanol added to the solution causes an increase in the efficiency of pyruvic acid ozonation. This indicated that a reaction occurs on the surface of the catalyst and follows the Langmuir–Hinshelwood mechanism, which is when both reactants adsorb on the surface of the catalyst, and after subsequent reaction, products are formed and desorb to bulk solution [112]. The same catalyst revealed very high catalytic activity in the process of ozonation of gallic acid [113]. Ozonation alone resulted in only 35% mineralization of organic carbon within 180 min reaction time and the usage of 150% of stoichiometrically required ozone. Catalytic ozonation resulted in 90% mineralization of organic carbon within the same time and the usage of only 25% of stoichiometrically required ozone dose. It was also reported that both ozonation alone and catalytic ozonation of gallic acid do not proceed via a radical pathway. However,

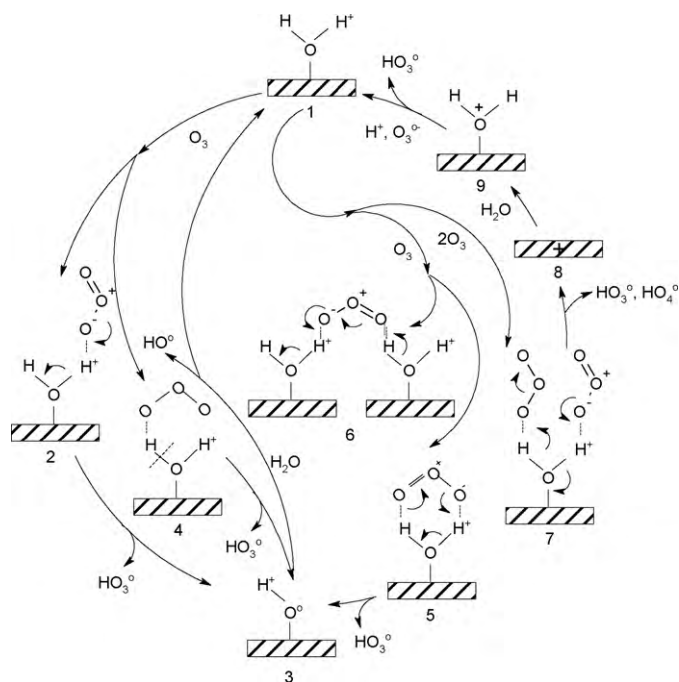
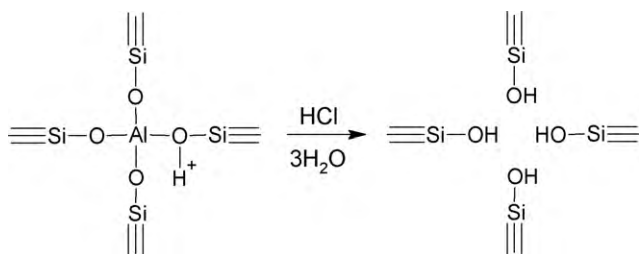


Fig. 5. Mechanism of ozone decomposition on the surface of ceramic honeycomb modified with metals (modified from [109]).

the presence of tert-butanol significantly decreased the mineralization of organic carbon in both processes, which indicates the importance of hydroxyl radicals in the decomposition of primary products of gallic acid ozonation [113]. Perovskite was also found to be an active catalyst in the ozonation of simulated phenolic wastewater [114].

Alumina and titania deposited on SiO_2 as well as zeolites NaX and 4A showed catalytic activity in the removal of phenol [115]. Additionally, no change of catalytic activity of the same zeolites in which cations were replaced with Co and Ni was observed, which indicates that an ion-exchange process is not necessary in order to observe catalytic activity of zeolites [115]. On the other hand dealuminated Y zeolite was active in the decomposition of ozone and ozonation of phenol. It was also observed that the catalytic process is radical in nature. The catalyst also revealed similar catalytic activity over several catalytic processes undertaken. Unfortunately lack of pH control during experiments undertaken in this work decreases the value of the report. No adsorption studies for phenol were also reported [116].

Valdés et al. [117] studied ozone decomposition in the aqueous solution promoted by zeolite and volcanic sand (composed of: SiO_2 , 63.7%; Al_2O_3 , 13.9%; Fe_2O_3 , 4.7%; N_2O , 3.8%; K_2O , 3.0%; CaO , 2.9%; MgO , 1.2%). It was observed that the use of zeolite and volcanic sand increased ozone decay rates, as compared to ozone natural self-decomposition, leading to greater free radical generation. The efficiency of ozone decomposition was found to be dependent on the pH of the solution and pH_{PZC} of the catalyst [117]. Furthermore, ozone decomposition in the presence of volcanic sand was found to be less affected by the presence of radical scavengers than ozone self-decomposition [118]. Additionally, modification of zeolite and volcanic material via HCl–hydroxylamine treatment resulted in a change in capacity of the two materials to decompose ozone. In the case of modified zeolite, the capacity to decompose ozone increased significantly, probably due to the increase of Lewis acid sites. It was suggested that zeolite underwent structural changes due to acid treatment with HCl resulting in aluminium expulsion in a soluble form and its replacement by a nest of four hydroxyl groups [118]:



This hypothesis is supported by the fact that pH_{PZC} decreased from initial 7.9 to 2.7. However, the acid treatment decreased volcanic sand activity in ozone decomposition, which was suggested to be associated with metal oxide leaching, as a significant decrease in Fe and Mn oxides content in modified volcanic sand was observed.

Natural brucite ($\text{Mg}(\text{OH})_2$, 94.7%; SiO_2 , 2.9%) and magnesite (brucite calcined at 450°C ; composition: MgO , 86%; SiO_2 , 3.7%; CaO , 1.4%; Fe_2O_3 , 0.7%; Al_2O_3 , 0.3%) were also studied as catalysts of ozonation of phenol [119]. Raw bauxite composed of boehmite ($\gamma\text{-AlOOH}$), kaolinite ($\text{Al}_2\text{Si}_2(\text{OH})_4$), quartz (SiO_2), of which $\gamma\text{-AlOOH}$ was a major component, was reported to be an effective catalyst for the ozonation of 2,4,6-trichloroanisole [120]. Bauxite's activity was found to be superior to other aluminium oxides such as $\gamma\text{-AlOOH}$, $\gamma\text{-Al}_2\text{O}_3$. In the presence of tert-butanol the efficiency of the catalytic system decreased which indicated that oxidation of 2,4,6-trichloroanisole is radical in nature. Only limited adsorption of the compound on bauxite was observed. The presence of NOM was found to inhibit hydroxyl radicals formation [120].

Aluminosilicates, especially those of low porosity and low Al content were also studied as potential catalysts of ozonation. Kim et al. [121] reported that microporous silicate of Si/Al ratio equalling 400 is active in the ozonation of pesticide dichlorvos. The same groups later established a new ozonation method utilising microporous high silica zeolites in the adsorption of ozone. Microporous high silica zeolites have the capacity to adsorb ozone due to hydrophobic properties of their pores. Ozone is a molecule of rather low polarity and therefore the non-polar environment increases its stability. The high efficiency of such a two-phase system was studied for several compounds and reported in a few papers [121–124]. The same group also studied high silica zeolites for the removal of 2-methylisoborneol (MIB), a compound of hydrophobic character [125–127]. The proposed mechanism is significantly different from others reported in the literature. It states that ozone is stabilised in high silica zeolites due to non-polar properties of ozone and its affinity towards non-polar phases. A similar phenomenon was utilised also in other two-phase ozonation systems discussed later on in this review.

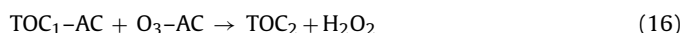
3.4. Activated carbon

It is well established that activated carbon used together with ozone can provide better removal of colour than when the two techniques are applied separately [128]. Similar results have been observed for the removal of phenolic compounds from water [129]. Jans and Hoigné [130] have proven that low mg quantities of activated carbon (or carbon black) can result in the decomposition of ozone in water leading to the generation of hydroxyl radicals. It was reported that the number of active centres on the surface of activated carbon capable of ozone decomposition is limited, but ozone decomposition and radicals formation is three times faster than in the absence of the catalyst. Therefore activated carbon can be considered as a catalyst of the ozonation process proceeding via radical pathways. Furthermore, Jans and Hoigné [130] reported that ozone decomposition occurs on the surface of activated carbon and

hydroxyl radicals formed react with organic molecules in the solution. However it was not revealed which active sites on the surface of activated carbons are responsible for ozone decomposition.

FTIR spectra obtained for activated carbons ozonated at different pH demonstrate absorption at 790 and 1102 cm^{-1} , which according to Beltrán et al. [131] can be attributed to vibrations of surface ozonide and peroxide ions respectively (interpretation of spectra was based on the work published by Bulanin et al. [132,133]). It is however questionable whether ozone adsorbed from aqueous solution can withstand the drying process. Beltrán et al. [131] also studied the kinetics of ozone decomposition and revealed that ozone decomposition occurs mainly at basic pH (6–9) and is catalysed by hydroxyl ions, which are adsorbed on the surface of the catalyst. This report confirms the hypothesis that hydroxyl radicals are formed mainly in the bulk solution and not as a result of surface interactions. In another paper, Beltrán et al. [134] proved that mineralization of oxalic acid at pH 2.5 during ozonation proceeds via a radical pathway and occurs in bulk solution. In contrast, Faria et al. [39] reported that mineralization of oxalic acid at pH 3 proceeds via reactions occurring on the surface of activated carbon and also in the bulk solution. Additionally, they revealed that the basicity of activated carbon is responsible for ozone decomposition reactions. A catalytic effect was observed for as low an amount as 0.5 g of the catalyst per one litre of solution. Furthermore, adsorption was found to play an important role in the observed catalytic effect of activated carbon during ozonation of carboxylic acids [39]. Similar results were observed by Sánchez-Polo and Rivera-Utrilla [40], who proved that activated carbons, which were not oxidised with ozone and are characterised by higher basicity, are more active catalysts in the process of 1,3,6-naftalenesulfonic acid ozonation. Another work by Beltrán et al. [135] reports much higher ozonation efficiency of pyruvic acid on activated carbon when compared with ozonation alone. Mineralization of pyruvic acid was found to be particularly high due to catalytic processes occurring. It was however reported [135] that a high catalyst dose accounting for 40 g/L was needed. Furthermore, catalytic reaction of ozone and pyruvic acid was zero order but it was not decided whether it proceeded via Langmuir–Hinshelwood or Eley–Rideal mechanisms. Additionally, the authors showed that at pH 7.5 both carbonates and tert-butanol influence the efficiency of the catalytic ozonation process, which suggests that hydroxyl radicals are the active species responsible for oxidation reactions. In another work, Beltrán et al. [136] studied the ozonation of gallic acid. It was reported that several by-products are formed: initially ketomalonic acid, oxalic acid and hydrogen peroxide and then these products are mineralised as a result of secondary radical reactions initiated via ozone decomposition on activated carbon. The formation of hydrogen peroxide was also reported by Gu et al. [137] during ozonation of p-nitrophenol.

Nitrobenzene is another chemical that can be effectively removed from water via catalytic ozonation. Ma et al. [138] reported that at pH 6 the process proceeds via radical reactions and is strongly tert-butanol dependent. Several activated carbons were also effective in the removal of diclofenac from water, with efficiency reaching 95% [139,140]. Adsorption of both ozone and organics on the surface of activated carbon (AC) was found to be an important step of diclofenac's ozonation [140]. According to Beltrán et al. [140] adsorbed organic compounds (diclofenac and its intermediates) react with adsorbed ozone to yield hydrogen peroxide (see reactions (14)–(16)):



where TOC_1 indicates TOC (total organic carbon) adsorbed on AC and TOC_2 indicates oxidised TOC_1 .

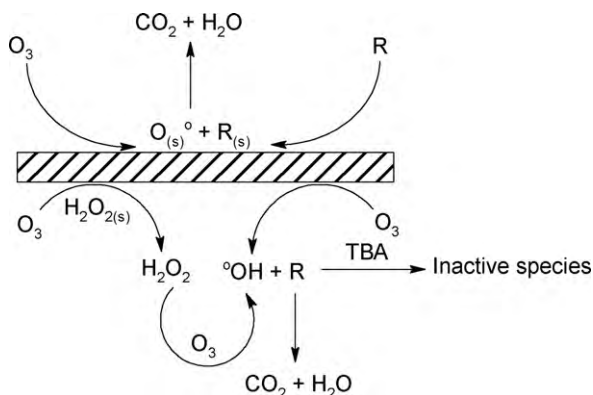


Fig. 6. Mechanism of catalytic ozonation of oxalic acid in the presence of MWCNT (R – oxalic acid; $O^*(s)$ – surface oxygenated chemicals; R_s – adsorbed oxalic acid modified from [146]).

Hydrogen peroxide can also be formed via ozone decomposition on the surface of activated carbon, but the contribution of this pathway to hydrogen generation was found to be limited in the overall efficiency of the system [140].

Surface reaction between adsorbed ozone and adsorbed hydrogen peroxide is proposed to yield hydroxyl radicals [140]:



Non-adsorbed organic matter reacts with hydroxyl radicals to finally yield inorganic carbon (see reaction (19)) [140]:



Activated carbons were also used as supports for metals and metal oxides. For example Ma et al. [138,141] reported that MnO_2/GAC revealed much higher catalytic activity during nitrobenzene ozonation than GAC [138]. It was also observed that higher efficiency of the process took place at lower pH (2.7–3.2) rather than higher pH (6.7–9.5). Furthermore, it was shown that the presence of a radical scavenger, tert-butanol, did not influence the efficiency of the process, which indicates that oxidative reactions do not proceed via radical reactions. Additionally, it was observed that adsorption of nitrobenzene on the surface of the catalysts plays an important role in the catalytic process.

Nickel oxide deposited on activated carbon was found to increase the efficiency of p-CBA ozonation leading to almost complete mineralization of the acid [142]. In other work, several metal oxides such as Ni, Fe, Co and Mn were deposited on activated carbon and studied as possible catalysts of phenol ozonation [143]. Pt deposited on graphite revealed high activity in the ozonation of oxalic acid. No decrease of catalytic activity was observed over a longer use [144]. Pt deposited on carbon nanotubes showed higher catalytic activity than Pt deposited on activated carbon. It was reported to decompose ozone (to an even higher extent than carbon nanotubes) with the formation of hydrogen peroxide and hydroxyl radicals, which are responsible for the degradation of oxalic acid [145].

Liu et al. [146] presented a mechanism of oxalic acid ozonation on multi-walled carbon nanotubes (MWCNT). Similarly to Faria et al. [39] and Beltrán et al. [134] the mechanism assumes radical chain reactions. According to the mechanism (Fig. 6) active $O^*(s)$ species are formed on the surface of the catalyst as a result of ozone decomposition and can represent any oxygen-containing active species (such as HO^\bullet). $O^*(s)$ species react with adsorbed organic molecules. Oxidative reactions take place also in bulk solution. The free radicals can be generated in two ways. In the first scenario MWCNT acts as an initiator in the transformation of ozone into

active species (such as hydroxyl radicals) in solution. In the second scenario, ozone reacts with surface groups of MWCNT to generate adsorbed hydrogen peroxide, which diffuses into bulk solution and reacts with ozone to yield hydroxyl radicals [146].

The above discussion indicates that also in the case of catalytic ozonation on activated carbon different mechanisms have been proposed. Some reports indicate radical processes, other prove that catalytic activity of activated carbon does not result from the capacity to generate hydroxyl radicals.

3.5. Non-polar systems enhancing ozonation

Ozone is a non-polar molecule characterised by a relatively low dipole moment of 0.46D, which is similar to dipole moments of aromatic hydrocarbons. It can be therefore suggested that ozone will have high solubility in non-polar organic solvents [147]. In a very polar solvent, such as water, ozone is very unstable and undergoes decomposition, which increases with an increase of pH. Due to the low polarity of ozone, non-polar organic solvents should not only increase its solubility but also increase its stability. High ozone solubility in non-polar solvents such as perfluorinated hydrocarbons or polydimethylsiloxane solvents has been already reported in several papers [148–154]. For example ozone solubility was found to be approximately 10 times higher in perfluorinated hydrocarbons than in water [148–150]. As a result, such a perfluorinated medium, which is immiscible with water and is resistant to ozone oxidative power, could serve as an ozone reservoir for reactions taking place in the aqueous phase or could be the site of reactions between both ozone and organics extracted from the aqueous phase. The idea of the usage of perfluorinated hydrocarbons as the reaction medium was proposed by Bhattacharyya et al. [148–150] and followed by Chang and Chen [151,152]. A detailed discussion of their work is presented elsewhere [11].

It is assumed that oxidation of organics in the two-phase non-polar ozonation systems utilising perfluorinated solvents proceeds via molecular ozone reactions. However, Gromadzka and Nawrocki [12] reported that oxidative reactions occurring during two-phase ozonation in the presence of perfluorinated hydrocarbons do not follow molecular ozone reactions pathways. The very effective removal of organics such as clofibrac acid, which are only effectively removed via radical chain reactions, was observed in a two-phase system. As the introduction of tert-butanol caused a decrease of two-phase ozonation efficiency, it was suggested that hydroxyl radicals (and not only molecular ozone) are responsible for oxidative reactions leading to clofibrac acid decomposition. Additionally, due to the very low solubility of clofibrac acid in the perfluorinated solvent, the oxidative reaction could only take place in the aqueous solution. To summarise, two-phase ozonation utilising non-polar solvents does not necessarily follow molecular ozone reactions pathway as was initially suggested. The phenomenon of a significant increase of ozone solubility and stability in perfluorinated medium was also applied in a two-phase ozonation system utilising perfluorinated acids, which were chemically bonded to the surface of alumina. A significant increase of ozonation efficiency of several organic contaminants such as: aromatic hydrocarbons, ethers, humic acids and natural organic matter was observed in a two-phase ozonation system utilising alumina or MCM-41 modified with perfluorooctanoic or perfluorooctadecanoic acids [48,49,155–160]. Two-phase ozonation in the presence of perfluorinated alumina was also utilised in the removal of dyes from water [161,162]. The application of other ozone-loaded solid media such as: silica gel [163] and high silica zeolites [121–126] were also reported. The utilisation of such ozone-loaded non-polar solid phases instead of the initially proposed non-polar liquid solvents allows for a more convenient possible application of two-phase ozonation systems in water treatment technology. Non-polar

Table 5
Two-phase ozonation.

Non-polar phase	Organic compound	Reference
Non-polar solvents Perfluorinated hydrocarbons	Phenol and chlorophenols, 2-naphtol, chlorendic acid, diclofenac, clofibric acid, sulfamethoxazole, dibutyl phthalate	[12,148–152,184]
Polydimethylsiloxane	Phenol, chlorophenols, chloro- and nitrobenzene, nitrotoluene	[153,154]
Non-polar solids Perfluorinated alumina, perfluorinated MCM-41 High silica zeolites	Aromatic hydrocarbons, ethers, humic acids, NOM, dyes Trichlorotoluene	[48,49,155–161] [123]

phases used in the two-phase ozonation processes are gathered in Table 5. The idea of the usage of non-polar media in ozonation of organic compounds is promising and should be investigated as it might lead to a much more effective utilisation of ozone in the removal of organic contaminants from water.

4. Conclusions

The main aim of catalytic ozonation processes is to increase the degradation of organic contaminants in water and additionally to lead to higher mineralization of these chemicals. These processes are also very often characterised by a lower usage of ozone when compared with ozonation alone. A decrease in the formation of bromates due to catalytic ozonation has been also confirmed. Despite a high number of papers published in this field, there is a lack of understanding of the mechanisms governing catalytic ozonation processes. Furthermore, due to the lack of understanding of processes responsible for both catalytic activity and also deactivation of catalysts, catalytic ozonation still remains in the sphere of laboratory experiments with only a few attempts at technological applications. The major problem lies in contradictory mechanisms governing catalytic process proposed by different research groups. Some authors suggest radical pathways involving ozone decomposition and hydroxyl radicals formation, others indicate that catalytic oxidation proceeds via different pathways, which do not involve hydroxyl radicals formation. Another important issue, which is vital in catalysis is adsorption of ozone and organics. It is still not clear how, or if, ozone adsorbs on the surface of the catalyst and whether this process leads to ozone decomposition followed by the formation of surface-bound or free radicals. It is also not known whether adsorption of organics on the surface of catalyst plays a crucial role in the catalytic process. Several authors reported high adsorption of organic molecules on catalysts, others indicated that this process is not required for efficient catalytic oxidation. Therefore it is of importance to standardise research efforts leading to an understanding of mechanisms governing catalytic ozonation. Among parameters crucial in such studies are:

1. The pH of solution. This parameter influences charge of surface (active) centres on the catalyst, charge of ionic or ionisable organic molecules and also charge of possible catalyst's poisons. Therefore pH is of vital importance as far as interactions between catalytic sites and organic molecules are concerned.
2. The nature of surface active sites responsible for catalytic reactions.
3. Adsorption of ozone. It is important to verify whether ozone undergoes adsorption and decomposition on the surface of the catalyst. If this is the case, what (active) species are formed and whether they are surface bound or released into bulk solution.
4. Adsorption of organic molecules. It has to be verified whether adsorption of organic molecules on the surface of the catalyst takes place as this affects mechanisms of oxidation pathways.
5. Influence of inorganic ions such as F^- , PO_4^{3-} , SO_4^{3-} , HCO_3^- , CO_3^{2-} ; on the efficiency of the catalytic ozonation processes.

These ions are commonly present in natural waters and due to their high affinity towards certain active catalytic sites they might block catalytic centres and work as poisons of catalysts. Phosphates, bicarbonates and carbonates are also radical scavengers.

6. Influence of natural organic matter on the efficiency of catalytic ozonation.
7. Stability of catalysts in a continuous application.

Finally, it should be also emphasised here that catalytic processes occurring during oxidation of organic molecules in aqueous solutions are very complex in nature and due to the complexity of catalytic reactions one has to take into consideration that standardized mechanisms might not be easily achievable.

An understanding of the mechanisms of catalytic ozonation is vital if catalytic ozonation is to be used on technological scale and should lead to synthesis of effective catalysts. It should be remembered that in the case of catalytic processes occurring in aqueous solutions, adsorption of water cannot be underestimated, as water molecules will always compete with ozone for catalytic sites such as Lewis centres or hydroxyls.

According to the most popular views in the catalytic ozonation literature Lewis centres and/or surface hydroxyls are commonly considered as the ozone decomposition sites. However these views neglect the competing adsorption of water molecules on these sites. In our opinion water seems to be a stronger Lewis base than ozone molecule and thus the displacement of H_2O by O_3 at Lewis site is unlikely. The same can be said about the affinity of surface hydroxyls to water and ozone molecules. Ozone molecule as a non-polar individual may adsorb on non-polar adsorption sites – in aqueous solution there would be no affinity of H_2O molecules to such sites. Such an assertion is currently speculative. However, there is some evidence suggesting that adsorption of ozone on both hydroxyl and Lewis centres does not occur and some evidence confirming adsorption of O_3 on non-polar surfaces.

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